Signatures of the classical transition state in atomic quantum spectra

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We perform quantum mechanically exact calculations of resonances in the spectrum of the hydrogen atom in crossed external fields and establish a close connection between the classical transition state in phase space and features in the quantum spectrum. By varying the external field strengths, structures are revealed which are surprisingly similar to the quantized energy levels of the classical electron motion in the vicinity of the saddle point obtained with an approximation of the potential. The results give clear evidence for signatures of the transition state in quantum spectra.

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I. INTRODUCTION

Transition state theory, which has its original applications in the theory of chemical reactions (see, e.g., [1, 2, 3]), can also be applied to many dynamical systems which evolve from an initial ("reactants") to a final state ("products"). The key concept is based on trajectories in the classical phase space of a dynamical system. In particular, regions of the phase space which identify the reactant side and those which represent the product side are introduced. Of special interest are trajectories that connect the reactant side with the product side, because they describe the "reaction." The theory postulates the existence of a minimal set of states which is passed by all of these "reactive" trajectories, and this set is called the transition state. The transition state has no intersection with a "nonreactive" trajectory, and therefore describes a *boundary* between reactants and products in the phase space.

Among the large number of applications of the transition state theory, it has also proven to be important for understanding the ionization mechanism of atoms. In the case of the hydrogen atom in an external electric field the "reaction" corresponds to the ionization. The potential of the system is plotted in Fig. 1 (solid red grid), in which the Stark saddle point is clearly visible. Classical trajectories describing an ionization must pass the saddle point, and therefore the transition state must be located in its vicinity. An early work by Clark et al. [4] can be regarded as a first step in discussing the ionization mechanism of the hydrogen atom in crossed electric and magnetic fields in this context. They used a quadratic expansion of the potential around the Stark saddle point (see Fig. 1, dashed blue grid) to calculate quasi-bound states confined to the vicinity of the saddle. Further progress was achieved by Jaffé et al. [5, 6] who discussed transition state theory for systems without time-reversal symmetry, and found the transition state of the planar (i.e., two-dimensional) hydrogen atom in crossed external electric and magnetic fields. With the help of meth-
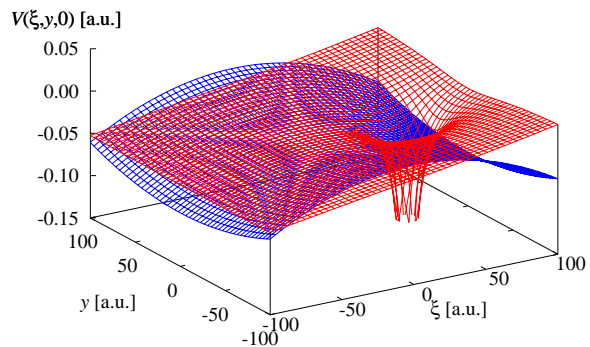

FIG. 1: (Color online) Potential of the hydrogen atom in an external electric field in the (ξ, y)-plane (cf. Eq. (2)) with $\xi = x - x_s$ denoted by the solid red grid. Reactive trajectories must pass the Stark saddle point at $(\xi = 0, y = 0)$ in whose vicinity the transition state is located. The dashed blue grid describes a quadratic approximation around the saddle point (cf. Eq. (3)).

ods from nonlinear dynamics Jaffé et al. [5, 6] discussed the chaotic ionization mechanism, and were able to explain the existence of electrons ionizing promptly and electrons ionizing with delay after repeated encounters with the core region. The problem that the practical applicability of transition state theory was restricted to low-dimensional systems was overcome by an algorithmic procedure which allows identifying the transition state in higher-dimensional systems [7, 8, 9], and is based on a normal-form representation of a power series expansion of the Hamiltonian. The quadratic approximation used by Clark et al. [4] coincides with the lowest order in the normal form expansion of the Hamiltonian introduced by Uzer et al. [7].

Even though the transition state for the hydrogen atom in crossed fields had been identified, the question of whether or not the classical trajectories in its vicinity leave a signature in the exact quantum spectrum remained unanswered since no such quantum spectra were

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available. We have succeeded in calculating these spectra, and it is the purpose of this paper to establish the close connection between the classical motion of an electron confined near the transition state and exact quantum resonances. To calculate the electron trajectories near the transition state we adhere to the simplest approximation and use the power series expansion of the potential around the Stark saddle point up to second order introduced by Clark et al. [4]. Higher orders would rapidly lead to a drastic increase of the computational effort, and, as will be seen from the results, the agreement of the quantized energy levels of the electron's motion with resonances in the quantum mechanically exact spectrum is already extremely good for the simple expansion. Thus, the expansion is completely sufficient to reveal the signatures of the transition state in the quantum spectrum.

The crossed-fields hydrogen atom is an ideal candidate to search for the connection between the classical transition state and its counterpart in a quantum system because the lowest-order approximations to the transition state as well as the quantum states are accessible with reasonable numerical effort. Chemical reactions with their large number of degrees of freedom are far more complicated and do not allow for the insight we gain in the case of the hydrogen atom, where only three degrees of freedom exist.

The paper is organized as follows. The system and the approximation around the saddle point are introduced in Sec. II. In Sec. III we present the results for the resonances. The calculation is performed for different external fields, which are varied such that lines in the two-dimensional space of the field strengths are traversed. This procedure will uncover close relations in the energies calculated with both methods. Finally, conclusions are drawn in Sec. IV.

II. HAMILTONIAN AND RESONANCES IN THE VICINITY OF THE STARK SADDLE POINT

The Hamiltonian of the hydrogen atom in crossed electric and magnetic fields is given, in atomic units, by

$$H = \frac{1}{2}\left(\boldsymbol{p} + \boldsymbol{A}\right)^2 - \frac{1}{r} + fx \,, \qquad (1)$$

where the electric field f is orientated along the x-axis and $\boldsymbol{A}$ represents the vector potential. The magnetic field is supposed to be oriented along the z-axis. In this case, usually the symmetric gauge $\boldsymbol{A} = -1/2(\boldsymbol{r} \times \gamma \boldsymbol{e}_z)$ with the magnetic flux density γ is used, whereas, for the approximated states discussed in this paper the application of the Landau gauge $\boldsymbol{A} = (-\gamma y, 0, 0)$ is more suitable. Besides the energy the parity with respect to the $(z = 0)$-plane is a good quantum number, which opens the possibility to consider states with even and odd z-parity separately.

A. Quadratic approximation

The transition state is located in the vicinity of the Stark saddle point, where the net electric force vanishes. For the potential caused by the external electric field and the nucleus,

$$V_f = -\frac{1}{r} + fx \,, \qquad (2)$$

the saddle point is located on the x-axis at $x_s = -1/\sqrt{f}$, and the saddle point energy has the value $V_f(\boldsymbol{r}_s) = -2\sqrt{f}$. The simplest approximation of the potential V_f which contains the structure of the saddle, is a quadratic expansion. This expansion leads to unbound solutions called "Quasi-Penning" resonances by Clark et al. [4] due to a formal similarity with the motion in a Penning trap. For the readers' convenience, we recapitulate the essential results. The expansion of the potential up to second order terms reads

$$V_f(\boldsymbol{r}) = -2\sqrt{f} - \sqrt{f}^3\xi^2 + \frac{1}{2}\sqrt{f}^3\left(y^2 + z^2\right) + \mathrm{O}((\boldsymbol{r}-\boldsymbol{r}_s)^3) \,, \qquad (3)$$

where $\xi = x - x_s$. The saddle structure of the potential has been visualized in Fig. 1, where the potential (3) is plotted in the (ξ,y)-plane. The comparison with the exact electric potential (2) shows clearly that the approximation is only valid close to the saddle point and can only describe states in its vicinity correctly.

With the gauge $\boldsymbol{A} = (-\gamma y, 0, 0)$ the Hamiltonian in the vicinity of $\boldsymbol{r}_s$ reads

$$H = \frac{1}{2}\left(p_\xi^2 + p_y^2 + p_z^2\right) - \gamma y p_\xi + \frac{1}{2}\gamma^2 y^2$$
$$- 2\sqrt{f} + \frac{1}{2}\sqrt{f}^3\left(y^2 + z^2 - 2\xi^2\right) \,, \quad (4)$$

and the eigenvalues of the quadratic potential yield the energy levels

$$E_{n_z,n_1,n_2} = -2\sqrt{f} + \omega_z(n_z + \frac{1}{2})$$
$$+ \omega_1(n_1 + \frac{1}{2}) + \omega_2(n_2 + \frac{1}{2}) \,, \quad (5)$$

where ω_z represents the frequency of the z-motion and is given by $\omega_z = f^{3/4}$. The separation of the coupled equations in the ξ- and y-directions with the help of an adequate canonical transformation [7], leads to one real oscillation frequency,

$$\omega_1 = \left\{\frac{1}{2}\left(\gamma^2 - \sqrt{f}^3 + \sqrt{\left(\gamma^2 - \sqrt{f}^3\right)^2 + 8f^3}\right)\right\}^{1/2} \,, \qquad (6)$$

and one imaginary decay rate,

$$\omega_2 = \mathrm{i}\left\{\frac{1}{2}\left(\sqrt{f}^3 - \gamma^2 + \sqrt{\left(\gamma^2 - \sqrt{f}^3\right)^2 + 8f^3}\right)\right\}^{1/2} \,, \qquad (7)$$

which describes the resonance character of the eigenstates. Thus, the resonance energies (real part of the complex eigenvalues) are completely determined by the two quantum numbers n_z, n_1 and read

$$\mathrm{Re}(E)_{n_z,n_1} = -2\sqrt{f} + \omega_z(n_z + \frac{1}{2}) + \omega_1(n_1 + \frac{1}{2}) \ . \quad (8)$$

B. Exact quantum calculations

The aim of this paper is to present evidence for the occurrence of quantum resonances corresponding to the classical transition state. For this purpose the approximate energy values (8) are compared with the results of exact quantum calculations. To perform the quantum calculations the Hamiltonian (1) is rewritten in dilated semiparabolic coordinates

$$\mu = \frac{1}{b}\sqrt{r+z} \ , \quad \nu = \frac{1}{b}\sqrt{r-z} \ , \quad \varphi = \frac{y}{x} \ , \quad (9)$$

where b is a convergence parameter. The transformed Schrödinger equation reads [10]

$$\left\{ \Delta_\mu + \Delta_\nu - \left(\mu^2 + \nu^2\right) + b^4\gamma\left(\mu^2 + \nu^2\right) \mathrm{i}\frac{\partial}{\partial\varphi} \right.$$
$$\left. - \frac{1}{4}b^8\gamma^2\mu^2\nu^2\left(\mu^2+\nu^2\right) - 2b^6 f\mu\nu\left(\mu^2+\nu^2\right)\cos\varphi \right\}\psi$$
$$= \left\{-4b^2 + \lambda\left(\mu^2+\nu^2\right)\right\}\psi \quad (10)$$

with

$$\Delta_\varrho = \frac{1}{\varrho}\frac{\partial}{\partial\varrho}\varrho\frac{\partial}{\partial\varrho} + \frac{1}{\varrho^2}\frac{\partial^2}{\partial\varphi^2} \ , \qquad \varrho \in \{\mu,\nu\} \ , \quad (11)$$

and the generalized eigenvalues $\lambda = -(1 + 2b^4 E)$, which are related to the energies E of the quantum states. We use a matrix representation of the full Schrödinger equation (10) in a complete discrete set of basis functions of the form

$$|N_\mu, N_\nu, m\rangle = |N_\mu, m\rangle \otimes |N_\mu, m\rangle \ , \quad (12)$$

where $|N_\varrho m\rangle$ are the eigenstates of the two-dimensional harmonic oscillator. Resonances are uncovered with the complex rotation method [11, 12]. Here, the coordinates $\boldsymbol{r}$ of the system are replaced with complex rotated ones $\boldsymbol{r}\mathrm{e}^{\mathrm{i}\vartheta}$, which leads to a complex symmetric matrix representation of the Hamiltonian. The complex rotation can be inserted in the transformed Schrödinger Eq. (10) with the help of the complex extended convergence parameter b

$$b = |b|\mathrm{e}^{\mathrm{i}\vartheta/2} \ . \quad (13)$$

Resonances appear as complex eigenvalues E, where the real part of E represents the energy and the imaginary part is related to the width $\Gamma = -2\mathrm{Im}(E)$.

With this method, the resonances of the hydrogen atom can be calculated with a high precision. It must be mentioned, however, that techniques for the matrix diagonalization used so far may fail in the energy region of interest. Former approaches to calculating the exact quantum resonances were mainly based on complex extensions of very efficient diagonalization algorithms for real symmetric matrices (see, e.g., Refs. [10, 13]) which require an orthogonality relation between all eigenstates. Of course, an orthogonality relation is not assured for non-Hermitian Hamiltonians and is, in particular, violated at so-called exceptional points, whose existence in the relevant part of the spectrum has been proven recently [14]. Exceptional points are branch point singularities of the resonances at which both the complex energies and the wave functions of two states become identical. In our calculations, the diagonalization was performed by applying the implicitly restarted Arnoldi method [15], which solves large scale sparse eigenvalue problems efficiently even for non-Hermitian Hamiltonians. The matrices were built up with a basis of about 10,000 states.

III. RESULTS AND DISCUSSION

To decide whether or not there is a connection between the classical motion around the saddle point and features in the exact quantum spectra, we compare the energy eigenvalues (8) with the exact quantum resonances. A coincidental agreement between two energies of both approaches for a *single* parameter value is always possible and does not answer our question. However, a connection between the approximation (8) and the quantum resonances is certainly present if the two results agree in a *larger region* of the parameter space. To check the connection we perform the calculations on lines $(f - f_0)/\gamma = \mathrm{const}$ in the two-dimensional parameter space spanned by the two field strengths, i.e., we introduce a parameter α and consider the field strengths $f(\alpha)$ and $\gamma(\alpha)$ as functions of α.

An example for a comparison is presented in Fig. 2(a) for states with even z-parity. Here, the resonances are calculated for different external field strengths on the line defined by

$$\gamma = 0.008 \times \alpha \ , \quad (14a)$$
$$f = 0.0003 \times \alpha \ , \quad (14b)$$
$$0 < \alpha < 1 \ , \quad (14c)$$

i.e., the ratio γ/f of the two field strengths is always constant. The solid blue lines represent the energy eigenvalues (8) of the quadratic approximation around the saddle point, and the red points are the numerically exact resonances of the Hamiltonian (1). The results show that for the lowest quantum numbers n_z, n_1 of the approximation there are very good agreements between both approaches on a large range of parameters α. The "Quasi-Penning"

FIG. 3: (Color online) Same situation as depicted in Fig. 2. The region around the avoided level crossings near the state with $n_z = 2$, $n_1 = 0$ is magnified.
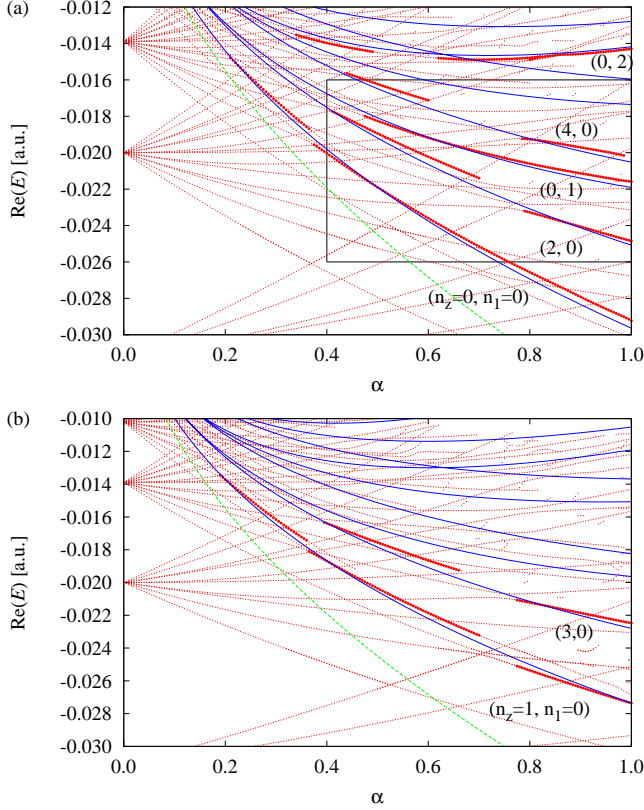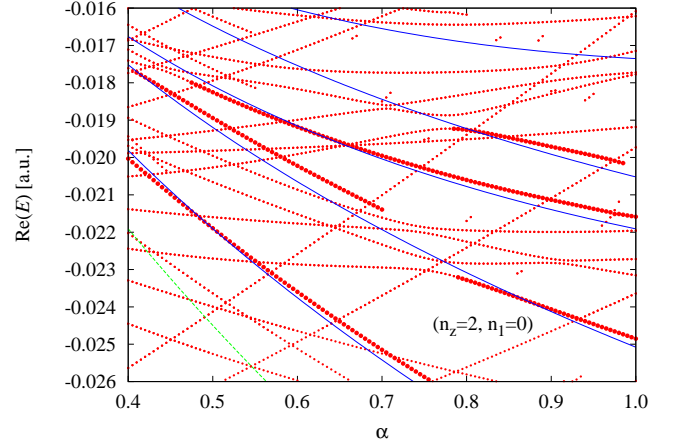

FIG. 2: (Color online) (a) Comparison of the quantized energies of the electron motion near the transition state (solid blue lines) with the exact quantum energies (red points) on the line $\gamma = 0.008 \times \alpha$, $f = 0.0003 \times \alpha$ for $0 < \alpha < 1$ as defined in Eqs. (14a)–(14c) in the (γ, f)-space for even z-parity. Only exact quantum energies with $|\text{Im}(E)| < 0.0006$ are shown. The exact resonances which trace the approximate energies (8) are shown by a larger line strength. The lowest (dashed green) line represents the saddle point energy. The black frame marks the region magnified in Fig. 3. (b) Same situation for states with odd z-parity.
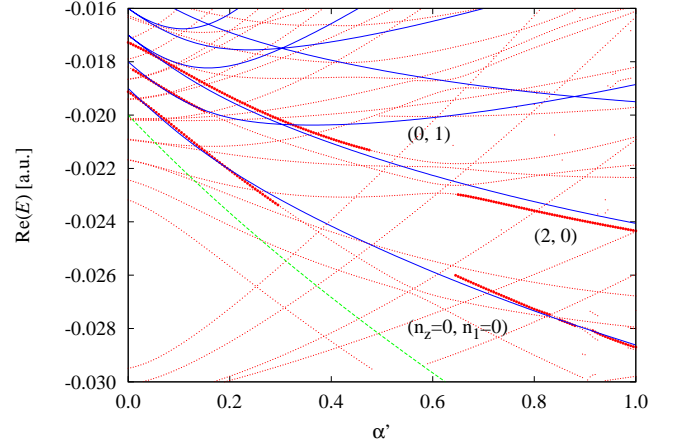
FIG. 4: (Color online) Same comparison of the quantized energies of the electron motion near the transition state (solid blue lines) with exact quantum energies (red points) as in Fig. 2 but on the line $\gamma = 0.01 \times \alpha'$, $f = 0.0001 + 0.0002 \times \alpha'$ for $0 < \alpha' < 1$ defined in Eqs. (15a)–(15c). Only exact quantum energies with $|\text{Im}(E)| < 0.0002$ are shown. The saddle point energy is marked by the lowest (dashed green) line.

resonances are traced by the quantum mechanically exact states when α is changed. Wherever this behavior is present, it is highlighted by a larger line thickness for the exact resonances.

Of course, the effect does also appear for odd z-parity, which is shown separately in Fig. 2(b) for the same physical parameters as in Fig. 2(a). As one can see, the agreement of the resonances is again very good in large regions of the parameter space.

There are, however, parameter values α for which a different behavior of the energy values exists. For low field strengths the Coulomb potential becomes too dominant, and the expansion of the potential in the vicinity of the Stark saddle point no longer leads to reasonable solutions, as can be observed in Fig. 2. Furthermore, avoided level crossings of the numerically exact resonances have no counterpart in the approximative states. Evidently, couplings of states, which are the origin of avoided level

crossings, are not included in the simple model. Thus, the deviations in these regions are not surprising. Fig. 3 shows an example of a region with avoided level crossings of quantum mechanically exact resonances. It can be clearly seen that far from the crossing the agreement between the numerically exact energies and the energy value corresponding to $n_z = 2$, $n_1 = 0$ in Eq. (8) is very good, whereas at the avoided crossings themselves the approximative solutions cannot reproduce the results of the full Hamiltonian (1).

The calculations shown in Fig. 4 are performed on the

TABLE I: Quantum numbers n_z and n_1 of the "Quasi-Penning" resonances closely related with exact quantum states.

n_z	n_1	n_z	n_1
0	0	4	0
1	0	0	1
2	0	0	2
3	0		

line

$$\gamma = 0.01 \times \alpha' \,, \tag{15a}$$
$$f = 0.0001 + 0.0002 \times \alpha' \,, \tag{15b}$$
$$0 < \alpha' < 1 \,, \tag{15c}$$

i.e., the ratio of the field strengths is no longer constant. For $\alpha' = 0$ there is still an electric field present but no magnetic field. The important property of this line is the existence of the saddle point for all values of α' drawn in Fig. 4. Again, there are exact quantum resonances which behave like the approximate solutions around the Stark saddle point and lead to a good agreement between both methods on a wide range of parameter values. Also near $\alpha' = 0$, where a pure Stark effect is present, the classical electron motion near the transition state describes the quantum resonances very well.

The calculations performed here reveal that a close connection between the two approaches exists. It appears for the seven pairs of quantum numbers of the "Quasi Penning" resonances listed in Table I. This rather high number of concordant resonances shows that, indeed, there is a signature of the classical transition state in the exact quantum spectrum.

IV. CONCLUSION

In summary we have demonstrated that there is clear evidence for the correspondence of classical motion of electrons confined to the vicinity of the Stark saddle point and resonances in the exact quantum spectra. The agreement of the energies in the classical transition state approach and the quantum calculations is very good. This appears surprising because the simplest expansion of the potential, only up to second order, was used, i.e., the approximation is only valid in a small region very close to the saddle point. This clearly can be understood as a sign for an eminent impact of the transition state on the exact quantum spectrum, and demonstrates the importance of the transition state for the ionization mechanism.

It must be noted, however, that the excellent agreement between both methods exists only for the real parts of the complex energy eigenvalues. The simple approximation used in the expansion of the potential is not capable of reproducing the correct decay rates or imaginary parts.

As an outlook, it seems worthwhile to extend the calculations to the normal form procedure developed by Uzer et al. [7] and to check whether higher orders can lead to an even better description of the quantum resonances by classical electronic motion. As can be expected, only the lowest "Quasi-Penning" resonances turn out to have a counterpart in the exact quantum resonances. It will be interesting to investigate which are the highest quantized levels of the transition state theory with a correspondence in the quantum spectrum.

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